

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 May 2001 (17.05.2001)

PCT

(10) International Publication Number
WO 01/34706 A1

(51) International Patent Classification⁷: C08L 83/04,
D06F 43/08, D06L 1/10

(74) Agents: SNYDER, Bernard et al.; General Electric Com-
pany, 3135 Easton Turnpike W3C, Fairfield, CT 06431
(US).

(21) International Application Number: PCT/US00/29263

(22) International Filing Date: 23 October 2000 (23.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/437,962 10 November 1999 (10.11.1999) US

(71) Applicant: GENERAL ELECTRIC COMPANY
[US/US]; 1 River Road, Schenectady, NY 12345 (US).

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA,
BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES,
FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG,
MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE,
SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU,
ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(72) Inventors: PERRY, Robert, James; 1 Milan Court,
Niskayuna, NY 12309 (US). KILGOUR, John, Alfred;
18 Royal Oak Drive, Clifton Park, NY 12065 (US).
DORN, Steven, B.; 54 Wiltshire Way, Niskayuna, NY
12309 (US).

(54) Title: PROCESS FOR REMOVAL OF ODORS FROM SILICONES

(57) Abstract: A process for removing malodorous elements from silicone dry cleaning solvents, comprising contacting the used
silicone solvent with adsorbent to remove the odor, and separating the silicone solvent.

PROCESS FOR REMOVAL OF ODORS FROM SILICONES

TECHNICAL FIELD

The present invention is directed to a process, more specifically, to a process for removing malodorous elements from silicone dry cleaning solvents.

BACKGROUND

Current dry cleaning technology uses perchloroethylene ("PERC") or petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments. Volatile siloxanes are being introduced into the dry cleaning industry as an alternative to PERC. However, undesirable odors are sometimes carried over with the siloxane solvent, so there exists a need to remove the odor from the siloxane solvent.

Methods for the purification of organopolysiloxanes have previously been reported as utilizing elemental metals (see US 5,245,067). Other patents disclose the purification of polyether silicones by contacting with an aqueous acid and removing the malodorous materials formed (see US 5,118,764), or the reaction with hydrogen and a hydrogenation catalyst (see US 5,225,509). Hexamethyldisiloxane has been purified by successive treatments with a condensation catalyst, washing with water, separating the phases, distilling the siloxane, treating with acid clay and then treating with activated carbon (see US 4,774,346). Siloxanes have also been purified by contacting with steam and distilling out the impurities (see EP 543 665). A deodorization method utilizing active carbon to which a functional group has been fixed through a silanol bond has been reported (see US 5,238,899). Finally, a method was reported for purifying silicone oil by adding a drying agent and an adsorption agent to silicone and passing a low water vapor inert gas through the system (see US 4,661,612).

There is a need for a method for removing unwanted odors in a volatile siloxane used in dry cleaning applications.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a method for removing malodorous elements from silicone dry cleaning solvents, comprising contacting the silicone solvent with adsorbent to remove the malodorous elements, and separating the silicone solvent.

The process of the present invention is effective in removing or reducing malodorous elements, such as for example, propionic acid, propionaldehyde, butyric acid and butyraldehyde, from the silicone solvent.

DETAILED DESCRIPTION OF THE INVENTION

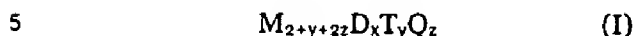
Preferably, the first preferred embodiment of the method of the present invention comprises, contacting a silicone dry cleaning solvent that may contain malodorous elements with an adsorbent, removing the malodorous elements, and separating the silicone solvent. Preferably, the silicone dry cleaning solvent is a volatile linear, branched, cyclic or a combination thereof, siloxane.

Compounds suitable as the adsorbent are those that effectively remove the malodorous components of the siloxane solvent. Examples of adsorbents suitable for use include, but are not limited to, silica gel, fullers earth, alumina, diatomaceous earth, magnesium silicate, granular activated carbon, molecular sieves, powdered decolorizing charcoal, magnesium sulfate, corn cob powder, zeolites, and clays. Preferably, the adsorbent is granular activated carbon, 4A molecular sieves, or 13X molecular sieves.

Compounds suitable as the linear or branched, volatile siloxane solvent of the present invention are those containing a polysiloxane structure that includes from 2 to 20 silicon atoms. Preferably, the linear or branched, volatile siloxanes are relatively volatile materials, having, for example, a

boiling of below about 300°C point at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more compounds of the structural formula (I):



wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

10 and Q is $SiO_{4/2}$

R^1 , R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and aromatic
15 hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example,
20 methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic rings per group, which may optionally be substituted on the one or more aromatic rings,
25 preferably with one or more (C₁-C₆)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-

trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenoxypropyl, biphenyloxypropyl.

In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent (C₁-C₆)alkyl radical, most preferably, methyl.

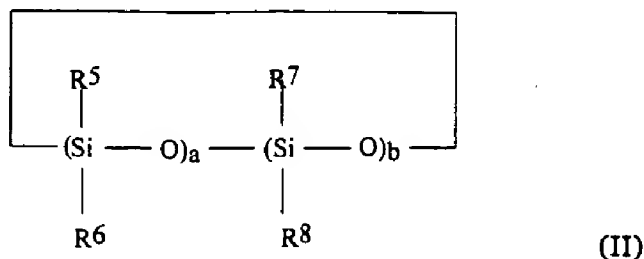
In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more of, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane or hexadecamethylheptasiloxane or methyltris(trimethylsiloxy)silane. In a more highly preferred embodiment, the linear or branched, volatile siloxane of the present invention comprises octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane. In a highly preferred embodiment, the siloxane component of the composition of the present invention consists essentially of decamethyltetrasiloxane.

Suitable linear or branched volatile siloxanes are made by known methods, such as, for example, hydrolysis and condensation of one or more of tetrachlorosilane, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or by isolation of the desired fraction of an equilibrate mixture of hexamethyldisiloxane and octamethylcyclotetrasiloxane or the like and are commercially available.

Compounds suitable as the cyclic siloxane component of the present invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the linear, volatile siloxanes and cyclic siloxanes are relatively volatile materials, having, for example, a

boiling point of below about 300°C at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the cyclic siloxane component comprises one or more compounds of the structural formula (II):



wherein:

R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group;
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

In a preferred embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of dimethyldichlorosilane and are commercially available.

In a first embodiment of the method of the present invention, approximately 100 parts by weight ("pbw") of siloxane solvent contacts up to about 100, more preferably up to about 50, even more preferably up to about 25 pbw of adsorbent for about 0.1 to about 6 hours, more preferably from about 0.1 to about 2 hours, even more preferably from about 0.1 to about 0.5 hours at a temperature of from about 10 to about 100 °C, more preferably from about 20 to about 60 °C in a batch mode.

In an alternative preferred embodiment of the present invention, siloxane solvent contacts a bed of adsorbent at a rate sufficient to provide efficient adsorption of the undesirable malodorous elements in a continuous mode, preferably at a ratio of from about 1 pbw siloxane solvent to about 1 pbw adsorbent (1:1), to about 10 pbw siloxane solvent to about 1 pbw adsorbent (10:1).

After the siloxane solvent has contacted the adsorbent for the appropriate time and the malodorous have been removed, the siloxane solvent can be recycled in the dry cleaning apparatus. The process of the present invention is effective in reducing the level of malodorous elements in the silicone solvent.

In a second embodiment of the process of the present invention, a dry cleaning fluid is treated by the process of the present invention.

The process of the present invention also comprises a dry cleaning process comprising the steps of: contacting an article with a silicone solvent, and removing the silicone solvent, then treating the silicone solvent that has been removed by contacting the silicone solvent with an adsorbent, and separating the silicone solvent from the adsorbent, then reusing the treated silicone solvent in the dry cleaning process.

The following examples illustrate the process of the present invention. They are illustrative and the claims are not to be construed as limited to the examples.

EXAMPLE 1

Cyclic siloxane (D_5) that was used as a dry cleaning solvent and had been reclaimed was treated to remove the odors. Approximately 100 grams of used siloxane solvent with odors was mixed with 25 grams of different adsorbents to form a slurry. The slurry was mixed for 6 hours at ambient temperature. The adsorbent was removed by filtration and the siloxane solvent evaluated olfactorally to determine the efficacy of the purification method. The results and adsorbents used are shown in Table 1 below.

The following adsorbents were used throughout the examples:

Adsorbent Number	Type of Adsorbent
A	Diatomaceous earth (Celite® 545)
B	4A molecular sieves
C	13X molecular sieves
D	silica gel 60-200 mesh
E	granular activated carbon
F	acid clay
G	$NaHCO_3$
H	Na_2CO_3
I	fullers earth
J	Powdered decolorizing charcoal (Norit®)
K	Powdered 13X molecular sieves

Table 1 – Odor Removal from Cyclic Siloxane – Long Contact Time

Exp. #	Adsorbent	Odor 1	Odor 2	Odor 3	Average Rating
1	None	1	1	1	1
2	A	1	1	2	1.3
3	B	3.5	4.5	4	4
4	C	4.5	4	5	4.5
5	D	3	2	3	2.7
6	E	5	5	5	5
7	F	1	1	2	1.3
8	G	1	1	1	1
9	H	1	1	1	1
10	I	2.5	2	3	2.5

The rating scale was as follows:

1 = no change

2 = small improvement

5 3 = some odor still present

4 = almost odorless

5 = no odor

Table 1 shows that 4A and 13X molecular sieves and granular activated carbon effectively removed the odors in the siloxane solvent.

EXAMPLE 2

A second set of experiments was run with a decreased contact time and a simulated in-line purification method. Used siloxane dry cleaning solvent was passed through a glass tube (approximately 1/2 inch diameter) containing various adsorbents. The purified siloxane solvent was again evaluated olfactorally to determine the efficacy of the purification method. The results and adsorbents used are shown in Table 2 below.

Table 2 - Odor Removal from Siloxane Solvent - Short Contact Time

Exp. #	Adsorbent	Amount of Adsorbent	Amount of Siloxane	Contact Time (minutes)	Odor
11	E	58 grams	200 grams	10	5
12	J	12 grams (with 24 grams filter aid)	200 grams	30	5
13	B	35 grams	200 grams	10	5

The same rating scale was used as in Example 1.

EXAMPLE 3

A similar experiment to that run in Example 1 was completed, substituting a linear siloxane solvent (MD₂M) for the cyclic siloxane. A sample of MD₂M was spiked with 10% of D₅ containing the malodorous elements. Table 3 shows the results of treating 200 g D₅ that was spiked with various odors (propionaldehyde (0.0145 g), propionic acid (0.0330 g), butyraldehyde (0.0210 g) and butyric acid (0.0353 g)) and then analyzing the samples olfactorally and via GC. Approximately 40 grams of linear siloxane solvent spiked with odors was mixed with 10 grams of different adsorbents to form a slurry. The slurry was mixed for 6 hours at ambient temperature. The

adsorbent was removed by filtration and the siloxane solvent evaluated olfactorally to determine the efficacy of the purification method. The results and adsorbents used are shown in Table 3 below.

Table 3 - Odor Removal from Linear Siloxane Solvent

Exp. #	Adsorbent	Amount of Adsorbent	Amount of Siloxane	Contact Time (hours)	Odor
14	E	10 grams	40 grams	6	3.3
15	J	10 grams	40 grams	6	4.7
16	B	10 grams	40 grams	6	2.7
17	C	10 grams	40 grams	6	4.3
18	D	10 grams	40 grams	6	3.0
16	"smelly" MD ₂ M solvent (control)	none	40 grams	-	1.0

5 The same rating scale was used as in Example 1.

EXAMPLE 4

Pure D₅ was spiked with various components (as shown in Table 4). Samples were run through adsorbents (10% adsorbent loading for 1 minute contact time). The samples were analyzed by GC to determine the efficacy of odor removal. Results are shown in Table 4.

5

Table 4 - Analysis of Spiked D₅ Samples.

Exp. #	Adsorb.	Propion-aldehyde	Propionic acid	Butyr-aldehyde	Butyric acid	Odor
17	None	73 ppm	165 ppm	105 ppm	176 ppm	1
18	J	<10 ppm	<10 ppm	<10 ppm	<10 ppm	4
19	C	<10 ppm	<10 ppm	<10 ppm	<10 ppm	4
20	E	9 ppm	46 ppm	31 ppm	53 ppm	3

The same rating scale as in Example 1 was used to determine the odor value.

10

The results were obtained from GC/MS data and are reported in ppm and are compared to the original loading of the control sample. The powdered decolorizing charcoal and the powdered 13X molecular sieves removed essentially all the contaminants as seen by GC/MS. The same conclusion was also determined olfactorally with a value of 4 on the odor scale. The granular activated carbon was less effective, getting a 3 on the odor scale and showing some residual acids and aldehydes remaining after treatment.

CLAIMS:

1. A process for removing malodorous elements from a silicone dry cleaning solvent, comprising contacting the silicone solvent with an adsorbent, and separating the silicone solvent from the adsorbent.

2. The process of claim 1, wherein the process is a batch process.

5 3. The process of claim 1, wherein the process is a continuous process.

4. The process of claim 2, wherein approximately 100 parts by weight of silicone contacts up to about 100 parts by weight of an adsorbent.

10 5. The process of claim 2, wherein the solvent contacts the adsorbent for about 0.1 to about 6 hours.

6. The process of claim 2, wherein the solvent contacts the adsorbent at a temperature of from about 10 to about 100 °C.

15 7. The process of claim 3, wherein the silicone solvent contacts the adsorbent at a ratio of from up to about 10 parts by weight of solvent to about 1 part by weight adsorbent.

8. The process of claim 3, wherein the solvent contacts the adsorbent for about 0.1 to about 6 hours.

9. The process of claim 3, wherein the solvent contacts the adsorbent at a temperature of from about 10 to about 100 °C.

20 10. The process of claim 1, wherein the adsorbent is granular activated carbon, 4A molecular sieves or 13X molecular sieves.

11. The process of claim 1, wherein the solvent is a linear or branched, volatile siloxane solvent of the formula:



wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2_2SiO_{2/2}$;

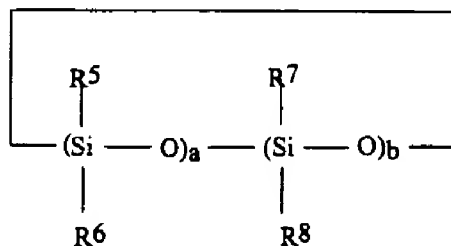
T is $R^3SiO_{3/2}$;

5 and Q is $SiO_{4/2}$

R^1 , R^2 and R^3 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

12. The process of claim 1, wherein the solvent is a cyclic siloxane of the formula:



wherein:

R^5 , R^6 , R^7 and R^8 are each independently a monovalent hydrocarbon group;

and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq$

15 $(a + b) \leq 10$.

13. The process of claim 12, wherein the cyclic siloxane consists essentially of decamethylcyclopentasiloxane.

14. The process of claim 1, wherein the malodorous elements removed from the solvent are propionic acid, propionaldehyde, butyric acid or butyraldehyde.

15. A silicone solvent treated by the process of claim 1.

16. An adsorbent used in the process of claim 1, wherein the adsorbent comprises malodorous elements selected from propionic acid, propionaldehyde, butyric acid and butyraldehyde.

5 17. A dry cleaning process comprising:

(1) cleaning an article by the steps of:

(a) contacting the article with a silicone solvent; and

(b) removing the silicone solvent; and

10 (2) treating the silicone solvent that has been removed by the steps of:

(a) contacting the silicone solvent with an adsorbent;

and

(b) separating the silicone solvent from the adsorbent.

15 18. The process of claim 17, further comprising reusing the treated silicone solvent in step (1).

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/29263

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L83/04 D06F43/08 D06L1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L D06F D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 309 166 A (MONCADA ALFONSO ET AL) 14 March 1967 (1967-03-14) column 1, line 23 - line 28 column 2, line 4 - line 7 column 2, line 57 - line 60 column 4, line 16 - line 27 claim 1	1-18
Y	US 3 203 754 A (YOUNG JOHN R ET AL) 31 August 1965 (1965-08-31) column 1, line 31 - line 37 column 1, line 52 - line 57 column 2, line 48 - line 50 column 6, line 25 - line 29 claim 7	1-18
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *A* document member of the same patent family

Date of the actual completion of the international search

15 February 2001

Date of mailing of the international search report

22/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentplan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tlx. 31 651 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

Hoepfner, W

Form PCT/ISA/210 (second sheet) (July 1992)

page 1 of 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/29263

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 658 459 A (GARTLAN JOHN A) 25 April 1972 (1972-04-25) column 1, line 18 - line 27 column 4, line 29 - line 36 claim 1 ---	1-18
Y	US 5 942 007 A (BERNDT DIETER R ET AL) 24 August 1999 (1999-08-24) column 2, line 31 - line 33 column 3, line 6 - line 22 claims 1,5 ---	1-18
Y	DE 39 40 804 A (KREUSSLER CHEM FAB) 13 June 1991 (1991-06-13) column 1, line 15 - line 24 column 1, line 38 - line 43 claim 1 -----	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

PCT/US 00/29263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3309166 A	14-03-1967	NONE	
US 3203754 A	31-08-1965	NONE	
US 3658459 A	25-04-1972	NONE	
US 5942007 A	24-08-1999	US 5865852 A	02-02-1999
		AU 4993599 A	07-02-2000
		AU 5101799 A	07-02-2000
		WO 0004221 A	27-01-2000
		WO 0004222 A	27-01-2000
		US 6063135 A	16-05-2000
		US 6042617 A	28-03-2000
		US 6056789 A	02-05-2000
		US 6042618 A	28-03-2000
		US 6086635 A	11-07-2000
		US 6059845 A	09-05-2000
DE 3940804 A	13-06-1991	GB 2238793 A, B	12-06-1991

Form PCT/ISA/210 (patent family annex) (July 1992)